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INTERPRETATION OF SOME REACTIONS IN THE CARBOHYDRATE FIELD IN TERMS OF CONSECUTIVE ELECTRON DISPLACEMENT

By Horace S. Isbell

ABSTRACT

An attempt has been made to show how the concept of consecutive electron displacement that has been developed in recent years may be used for the interpretation of certain reactions in the carbohydrate field. The viewpoint in general is that the peculiar properties of systems involving double bonds may be explained by the migration of electron pairs in the molecule from points of high electron density to points of lower electron density, with the addition and elimination of ions. A number of apparently unrelated complex reactions of the carbohydrates are considered and it is shown that the formation of the products may be explained by a few simple reactions involving shifts of electron pairs; these include enolization, de-enolization and double decomposition. Mechanisms are presented for the formation of the four classes of saccharinic acids from the 1,2-, the 2,3-, and the 3,4-enediols, for the formation of diacetylkojic acid from acetylglucosone, for the formation of unsaturated lactones from hydroxy acids, for the conversion of triacetylgucal to diacetylpseudoglucal, for the conversion of tetramethyl-1, 2-glucoseen to ω-methoxymethylfurfural, and for the formation of furfural and levulinic acid.

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I. INTRODUCTION

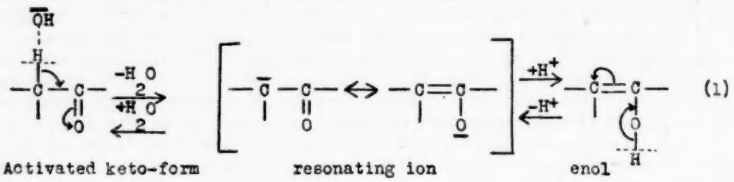
The development of physical organic chemistry in recent years has led to a type of organic chemistry in which reactions are represented in terms of the changes in the electronic structure of the reacting substances. Classical organic chemistry has thus been amplified, and an insight has been gained into the forces causing and controlling reactions. Although the fundamental principles of this approach to organic chemistry have been presented in a number of texts [1, 2, 3],[1] application in the field of carbohydrate chemistry has not been exten-

[1] Figures in brackets indicate the literature references at the end of this paper.

sive, and it is therefore of interest to examine some reactions of carbohydrates from the standpoint of the electronic changes involved. The mechanisms are presented not as established facts but rather as interpretations based on present concepts for the mechanisms of simple organic reactions. Although the examples chosen for consideration are highly complex, they seem to include only a few relatively simple changes such as enolization, de-enolization (ketonization), and displacement reactions.

Nearly all of the reactions discussed in the paper are preceded or accompanied by the formation of intermediate complexes which facilitate the addition and removal of groups, and the electronic changes indicated by the curved arrows. In the equations which follow, the dotted line connecting two groups is used to indicate the formation of an intermediate complex. The dotted line separating two groups represents the point of cleavage, whereas the curved arrow indicates the displacement of electrons under the influence of the attacking reagent. Presumably the reactions considered are of the ionic type rather than of the nonionic, or free radical type.

According to present concepts, the enolization of a carbonyl compound in alkaline solution, equation 1, may be considered to consist in



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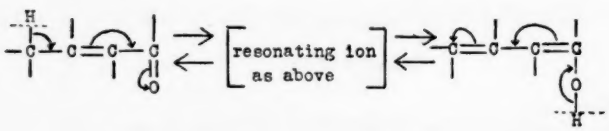

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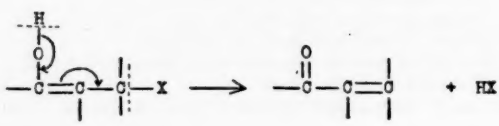

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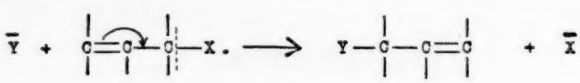

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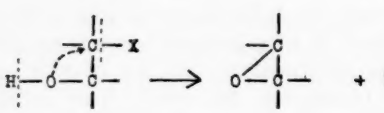

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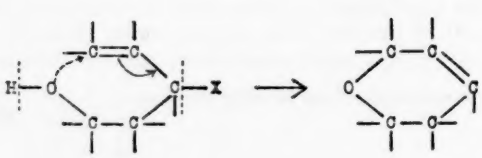


(6)

the formation of an activated complex between the base (usually a hydroxyl ion) and the hydrogen of the carbon adjacent to the carbonyl group, or at the end of a conjugated double-bond system. A flow of electrons in the activated complex, from the carbon-hydrogen bond to the carbon-carbon bond and from the carbonyl carbon to the oxygen, yields a resonating enolic ion. This ion picks up a proton from the environment and thereby forms either the enol- or the keto-tautomer. In case the system contains conjugated double bonds, the slightly polarized hydrogen attached to the carbon at the end of the conjugated chain combines with the base and enolization takes place as represented by equation 2.

De-enolization (ketonization) ordinarily takes place by ionization of the enolic hydrogen accompanied by a flow of electrons to the adjacent carbon, or if the enol contains a conjugated double-bond system, to the carbon at the end of the double-bond system. Electrical neutrality is maintained by the addition of a proton, or by elimination of a group carrying the excess electrons. The first process is the reverse of enolization, the second process is represented by equation 3, in which X is a group such as OH, Cl, OCH_3, OAc, etc., attached to the carbon adjacent to the enolic grouping, or to the carbon at the end of a conjugated double-bond system. Elimination of negative groups may also take place by displacement as represented in equation 4, or in some cases with the formation of heterocyclic rings, as in equations 5 and 6.

Changes of the type represented by the equations involve consecutive electron displacements with the addition and elimination of ions. The reaction mechanisms are similar to mechanisms which have been postulated by Hauser in fundamental studies relating to elimination and rearrangement reactions [4]. In a previous publication [5] the present author discussed briefly the alkaline cleavage of certain glycosides, the formation of benzene derivatives from ketoinositols, and the production of furfural from glycoseens. Limitations of space, however, did not permit full development of the subject, and consideration of many other important reactions.

II. FORMATION OF SACCHARINIC ACIDS BY THE ACTION OF ALKALI ON SUGARS

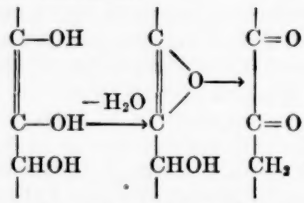
For many years the conversion of reducing sugars to saccharinic acids by the action of strong bases has been the subject of much speculation and considerable research. Recently an excellent review of the reactions resulting in saccharinic acids, and the work which led to the assignment of structures to the various saccharinic acids was published by Evans [6]. In the hexose series the saccharinic acids have been classified in four groups [7, 8]:

1. Metasaccharinic acids, $CH_2OH.CHOH.CHOH.CH_2.CHOH.COOH$.
2. Saccharinic acids $CH_2OH.CHOH.CHOH.\overset{COOH}{COH}.CH_3$.
3. Isosaccharinic acids $CH_2OH.CHOH.CH_2.\overset{COOH}{COH}.CH_2OH$.
4. Parasaccharinic acids $CH_2OH.CHOH.\overset{COOH}{COH}.CH_2CH_2OH$.

On account of the complex character of the substances, the idea was promoted early that they might be formed by recondensation of degradation products of the sugar molecule, such as lactic acid and

glyceraldehyde. This process would not be restricted to the formation of saccharinic acids containing the same number of carbons as the parent sugar; hence one would expect to obtain 6-carbon saccharinic acids from the lower sugars as well as from the hexoses. Since this is not the case, the hypothesis has been generally discarded.

Nef [7] postulated a progressive migration of the carbonyl group along the carbon chain with the formation of 2- and 3-ketohexoses. He assumed that these ketoses, by internal oxidation and reduction, form desoxydiketo compounds, which undergo benzilic acid rearrangements. According to Nef's concept, the desoxydiketo compounds were formed through intermediate methylenic compounds containing an active bivalent carbon atom. In the light of our present knowledge, Nef's mechanism for the production of the diketo compounds seems improbable, but his concept of the occurrence of a benzilic acid rearrangement is nevertheless acceptable. Benoy and Evans [9] suggested the following mechanism for the formation of the desoxydiketo compounds from enediols:



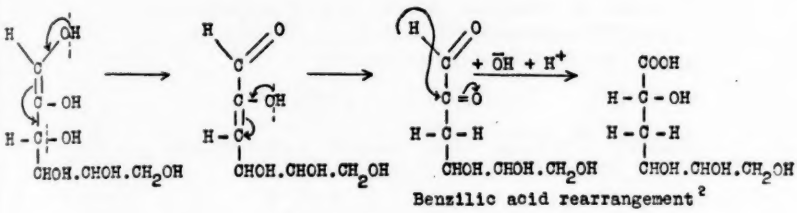
They consider the saccharinic acids to be derived from the 1,2-enediols, the isosaccharinic from the 3,4-enediols, and the parasaccharinic and metasaccharinic acids from the 2,3-enediols.

Nicolet [10] observed that α-hydroxy-β-methoxy-β-phenylpropiophenone, on treatment with alkali, gives α, β-diphenyllactic acid. He noted that the reaction requires elimination of the methoxyl attached to the beta carbon and stated that the reaction made a revision of Nef's theory of saccharinic acid formation necessary. Elimination of a methoxyl (or of a hydroxyl) on the carbon beta to a carbonyl group might take place directly by elimination of the elements of methyl alcohol (or water) from adjacent carbon atoms, or indirectly through enolization and a reaction of the type represented by equation 3, page 46. The latter course seems the more probable and is used in the equations for saccharinic acid formation, although it is recognized that either course might be followed.

The formation of the various saccharinic acids from the several enediols may be explained in accordance with the concept of consecutive electron displacement, by the following reactions: 1. Ionization of a hydrogen of the enediol followed by elimination of a hydroxyl by a reaction of the type represented by equation 3, page 46. 2. Ketonization with the formation of a desoxydiketo compound. 3. A rearrangement of the benzilic acid type, giving the saccharinic acid. The benzilic acid rearrangement, originally suggested by Nef, involves a shift of a group with its binding electrons from one carbon to another, and differs fundamentally from the consecutive electron displacements characteristic of most of the reactions considered here. Presumably it takes place through an intermediate ion formed either by addition of a hydroxyl, or by loss of a proton from the hydrated carbonyl group. The mechanism for reactions of the benzilic acid type (see footnote 2) is discussed in references [1, 2, 3, 4]. It may be ob-

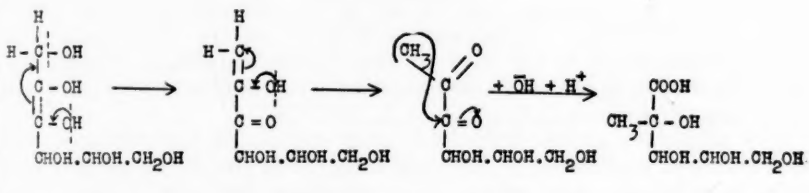
served by inspection of the accompanying formulas that metasaccharinic acids are represented as derived from the 1,2-enediols, parasaccharinic acids from the 3,4-enediols, and saccharinic and isosaccharinic acids from the 2,3-enediols. These correlations are at variance with those heretofore postulated. Reactions of the type outlined in the formulas may be used to account for the formation of saccharinic acids from other sugars and for the formation of lactic acid from glyceraldehyde through the intermediate methylglyoxal.

Formation of metasaccharinic acids from hexose 1,2-enediols



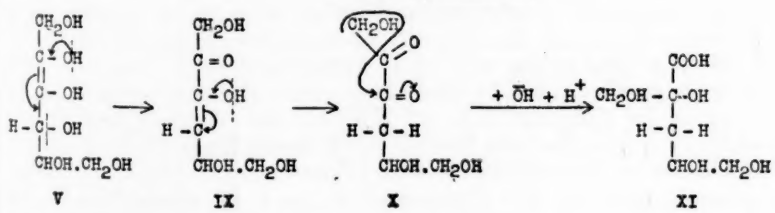
I II III IV

Formation of saccharinic acids from hexose 2,3-enediols



V VI VII VIII

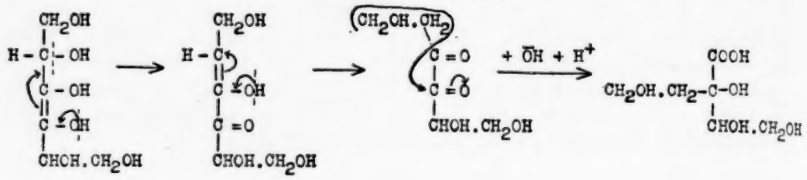
Formation of isosaccharinic acids from hexose 2,3-enediols.



V IX X XI

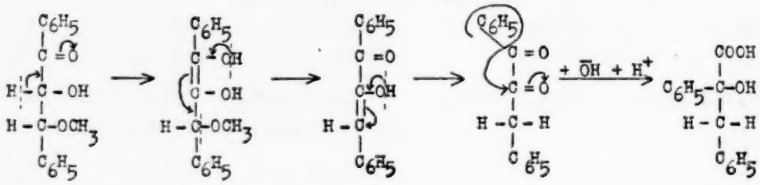
[2] In the benzilic acid rearrangement reported here, the hydrate and its ion, supposedly formed as intermediates in the reaction, are not given.

Formation of parasaccharinic acids from hexose 3,4-enediols



XII XIII XIV XV

Nicolet's conversion of α-hydroxy-β-methoxy-β-phenylpropiophenone to α,β-diphenyllactic acid may be formulated as follows:



XVI XVII XVIII XIX XX

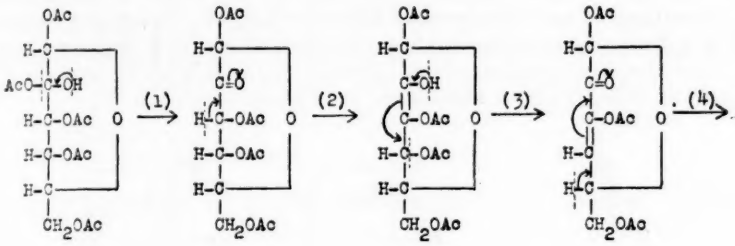
III. FORMATION OF DIACETYLKOJIC ACID FROM ACETYLATED GLUCOSONE HYDRATE

When tetraacetylglucosone hydrate is treated with acetic anhydride and either sodium acetate or pyridine, it is converted to diacetylkojic acid [11]. The experimental conditions are similar to those which effect the conversion of pentaacetylketoinositol to tetraacetoxybenzene [12] discussed in [5], and to the conditions which Barnes and Tulane have found to be effective for converting α-hydroxyketones into diacetates of enediols [13].

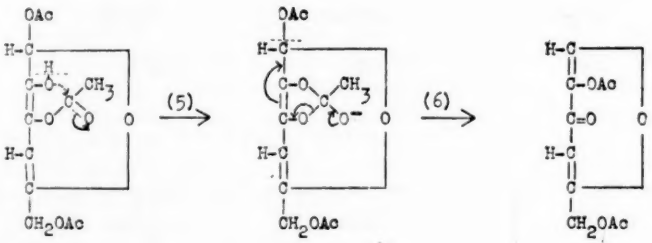
The action of acetic anhydride and sodium acetate in effecting enolization of keto acetates seems analogous to the catalytic action of bases and amphoteric solvents in effecting ordinary enolizations. Reactions involving the addition and elimination of protons are promoted by substances capable of donating and accepting protons, whereas reactions involving the addition and elimination of acetate ions seem to be promoted by substances capable of supplying and accepting acetate ions.

Maurer, who discovered the reaction leading to the formation of kojic acid, suggested a mechanism that includes the formation of a 2,3-anhydro compound, cleavage of the anhydro compound with the formation of a keto group at carbon 3, followed by elimination of 2 molecules of acetic acid. In accordance with the electronic concept as illustrated by formulas XXI to XXVII, the reaction may be explained by (1) formation of a free carbonyl group from the hemiacetal, (2) enolization of the carbonyl group, (3) de-enolization of the enediol with elimination of the acetyl group of carbon 4, (4) enolization of the resulting compound through the conjugated double bond, (5) and (6) migration of the acetyl group of carbon 3 to carbon 2 by means of an

intermediate complex of the orthoester type, with elimination of a proton and an acetate ion. The product would then be diacetylkojic acid, the substance obtained experimentally by Maurer. Many examples of the migration of acetyl groups in partially acetylated carbohydrates are reported in the chemical literature [14].



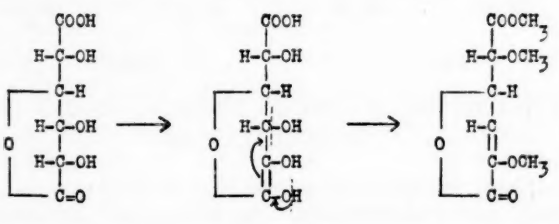
XXI XXII XXIII XXIV



XXV XXVI XXVII

IV. FORMATION OF UNSATURATED LACTONES FROM HYDROXY ACIDS

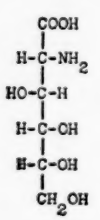
As pointed out by Kiliani [15], Rehorst [16], and others, the lactones of mannosaccharic and saccharic acids are peculiar in that they give a series of reactions not in accord with the simple lactone structure XXVIII. The lactones react with hydrogen cyanide, combine with iodine and give other reactions indicative of an unsaturated structure. To explain the existence of lactone salts differing from those of the corresponding acids, Haworth [17] proposed an enolic structure. The capacity of carboxylic acids, lactones, and esters to form enolic intermediates provides a means for forming unsaturated derivatives



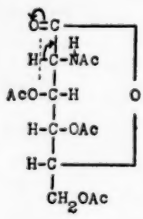
XXVIII XXIX XXX

of diverse character by processes of consecutive electron displacement. The formation of the unsaturated ester XXX by methylation of the monolactone of saccharic acid XXVIII and the formation of the dimethylester of dimethoxymuconic acid [18] were considered briefly in [5].

A somewhat similar explanation may be advanced to account for the formation of an unsaturated lactone XXXVI from glucosaminic acid XXXI by treatment with acetic anhydride and sodium acetate [19]. In the acetylation of chitobionic acid XXXVII the reaction stops with XXXVIII, a substance analogous to XXXIV.



XXXI



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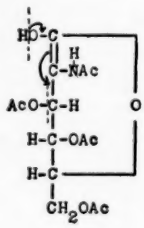

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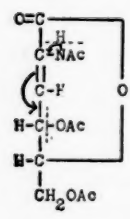

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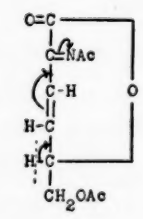
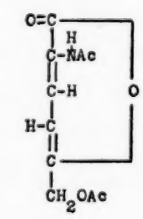
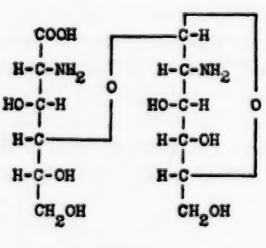


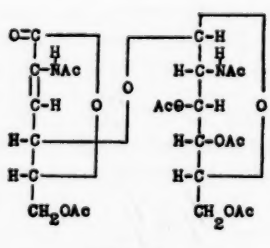
XXXV



XXXVI



XXXVII

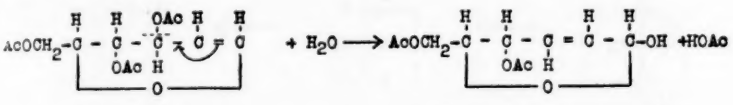


XXXVIII

V. CONVERSION OF TRIACETYLGLUCAL TO DIACETYL-PSEUDOGLUCAL

The glycals and related compounds give several reactions of interest to the subject under discussion. As discovered by Bergmann and Schotte [20] when the unsaturated sugar derivative, triacetyl-*D*-glucal, XXXIX is heated with water the double bond migrates from

the 1,2 to the 2,3 position and a compound designated diacetylpseudoglucal XL is formed. The reaction involves the addition of a hydroxyl ion and the elimination of an acetate ion, presumably with an electron shift, as indicated by arrows shown in the formula below. This is a simple example of a reaction of the type represented by equation 4, page 46.

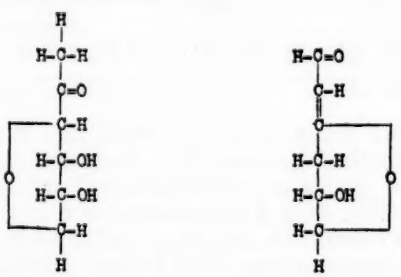


(triacetylglucal) XXXIX

(diacetylpseudoglucal) XL

VI. CONVERSION OF PSEUDOGLUCAL TO ISOGLUCAL AND PROTOGLUCAL

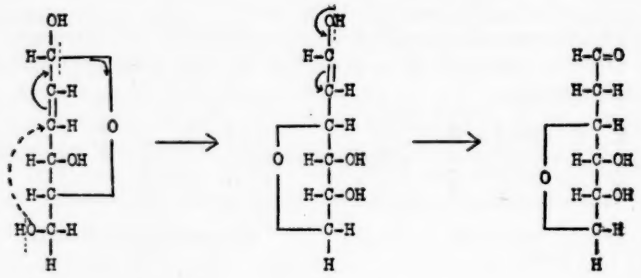
Bergmann and Freudenberg [21] have shown that saponification of diacetylpseudoglucal XL by treatment with cold alkali yields two products, designated isoglucal, XLI, and protoglucal, XLII. Attempts to work out a satisfactory mechanism for the production of these substances by means of consecutive electron displacements have been unsuccessful. Displacement reactions of the type under consideration would yield among other substances, by the processes indicated below, compounds having structures XLV and XLVIII. These hypothetical substances would give most but not all of the reactions recorded for isoglucal and protoglucal. Structures XLI and XLII for isoglucal and protoglucal are based on substantial experimental evidence [22], yet the plausibility of the hypothetical reactions leading to substances having structures XLV and XLVIII would seem to warrant further investigation.



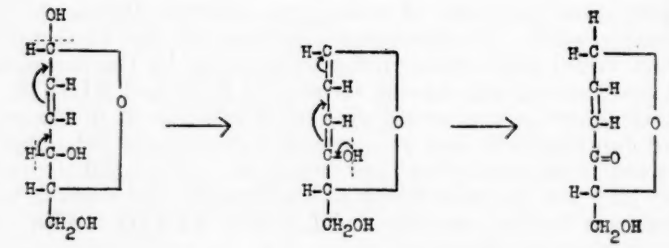
XLI (isoglucal) XLII (protoglucal)

The hypothetical reaction for the conversion of pseudoglucal XLIII to a 3,6-anhydro compound XLIV is similar to the intramolecular cleavage suggested previously [23] in explanation of the observation by Ohle and Wilcke [24] that 3,6-anhydro-β-methyl glucoside is formed by the action of sodium methylate on 2,3-anhydro-β-methyl alloside. The intramolecular cleavage represented in XLIII takes place through a double-bond system, whereas that giving 3,6-anhydro-β-methyl glucoside takes place directly. The migration of anhydro rings by successive electron displacements may occur in other reactions, for instance as an intermediate step in the formation of 1,6-anhydro compounds from β-phenyl glycosides [25].

HYPOTHETICAL REACTIONS OF PSEUDOGLUCAL



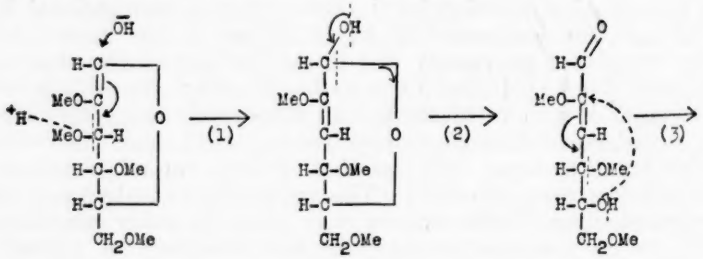
XLIII (pseudoglucal) XLIV XLV



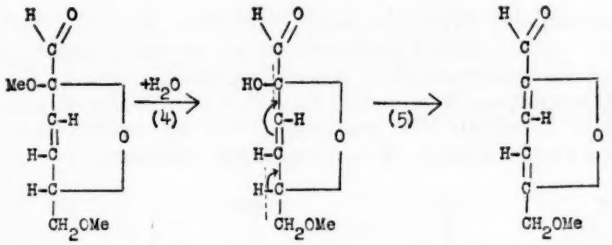
XLVI (pseudoglucal) XLVII XLVIII

VII. CONVERSION OF TETRAMETHYL-1,2-GLUCOSEEN TO ω-METHOXYMETHYLFURFURAL

Recently Wolfrom, Wallace, and Metcalf [26] made the very interesting observation that tetramethyl-1,2-glucoseen, XLIX on mild treatment with acid yields ω-methoxymethylfurfural LIV with the intermediate production of a 3,4-unsaturated osone LIII. The formation of the latter substance may be explained by the series of successive electron displacements outlined below. Presumably, the driving force of the reaction is the combination of the methoxyl group with hydrogen ions to form methyl alcohol.



XLIX LI

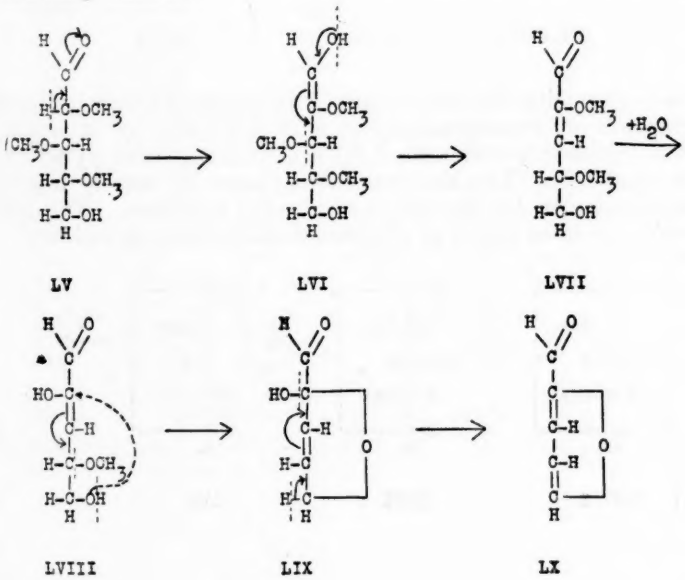


LII LIII LIV

Step (1) is a reaction analogous to the formation of diacetylpseudoglucal from triacetylglucal, (2) gives the open-chain modification, (3) is a reaction of the type represented by equation 6, page 46, in which the oxygen of carbon 5 provides the entering group, (4) gives rise to the 3,4-unsaturated osone isolated by Wolfrom, Wallace, and Metcalf, and (5) depicts its conversion to ω-methoxymethylfurfural. Hydrolysis of compound LII to the 3,4-unsaturated osone is shown as preceding the formation of ω-methoxymethylfurfural LIV. The latter substance might be formed directly from LII by elimination of the hydrogen of carbon 5 and the methoxyl of carbon 2, with the requisite electron shift.

VIII. FORMATION OF FURFURAL FROM TRIMETHYLPENTOSES

Several years ago Neher and Lewis [27] observed that when a trimethylpentose LV, represented here in the open-chain form is treated first with alkali and then with acid, furfural LX is formed even at room temperature, and suggested that the methylated enediol LVI produced by the action of the alkali on the methylpentose is the precursor of the furfural. In accordance with the concept of consecutive electron displacement, the reaction may be represented in the following manner:

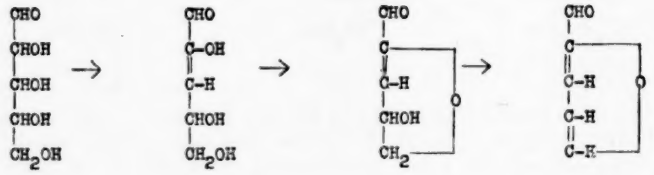


LV LVI LVII

LVIII LIX LX

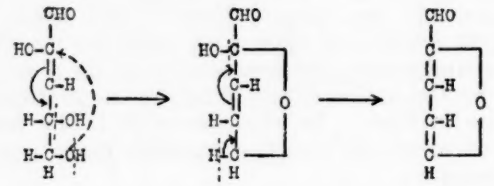
The mechanism, which is similar to that proposed for the conversion of tetramethyl-1,2-glucoseen to ω-methoxymethylfurfural, includes as an intermediate a 3,4-unsaturated osone LIX analogous to LIII, the compound prepared by Wolfrom, Wallace, and Metcalf.

Hurd and Isenhour [28] suggested the following mechanism to account for the formation of furfural from pentoses:



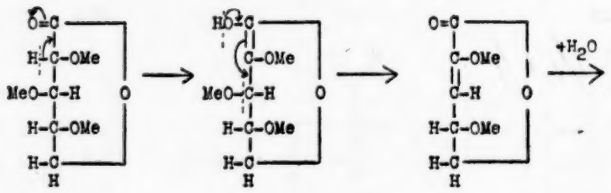
LXI LXII LXIII LXIV

Compound LXII corresponds to the methylated compound, LVII. In accordance with general principles employed here, LXII, on ring closure, would yield the 3,4-unsaturated compound LXVI in place of the 2,3-unsaturated compound LXIII suggested by Hurd and Isenhour. Furfural, LXVII, would result from the changes indicated by the arrows in formula LXVI. The driving force of the reaction would appear to be removal of hydroxyl groups through combination with hydrogen ions derived from the acid catalyst.

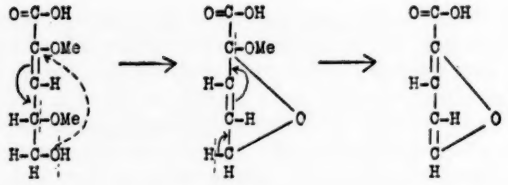


LXV (LXII) LXVI LXVII

In connection with the formation of furfural from trimethylpentoses, the formation of furanecarboxylic acid LXXIII by treatment of 2,3,4-trimethyl-δ-xylonolactone LXVIII with aqueous pyridine may be mentioned [29]. The reaction takes places by merely heating an aqueous solution of the methyl lactone with pyridine. The reaction may be explained in terms of electron displacement as follows:



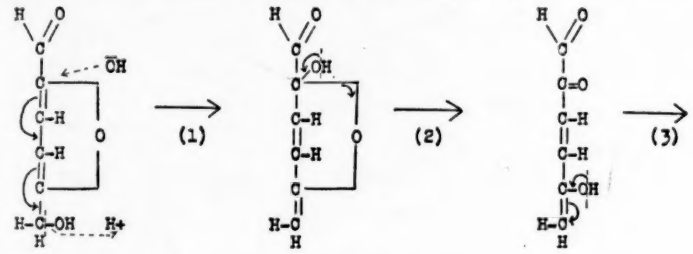
LXVIII LXIX LXX



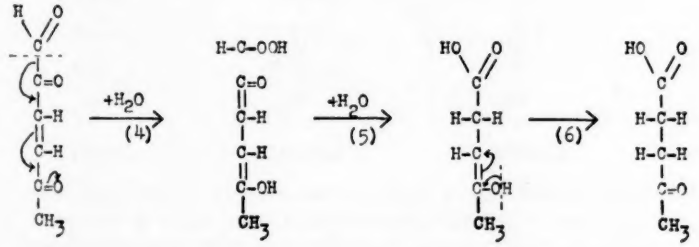
LXXI LXXII LXXIII

IX. FORMATION OF LEVULINIC ACID FROM ω-HYDROXYMETHYLFURFURAL AND FROM 2-DESOXYPENTOSES

When hexoses are boiled with aqueous acid ω-hydroxymethylfurfural is formed and ultimately converted to levulinic acid.[3] Considerable work has been conducted with the object of clarifying the mechanism for the formation of levulinic acid [30]. According to Pummerer, Guyot and Birkofer [30a] the reaction involves opening of the furane ring with the formation of 2,5-dioxo-6-hydroxycaproic aldehyde, followed by elimination of formic acid and oxidation of the aldehyde group by the primary alcohol group. The production of levulinic acid LXXX from ω-hydroxymethylfurfural LXXIV may be formulated in accordance with the electronic concept as follows:



LXXIV LXXV LXXVI

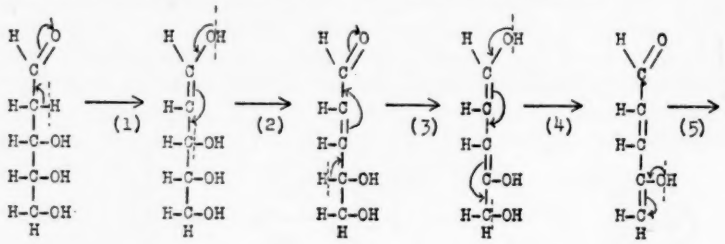


LXXVII LXXVIII LXXIX LXXX

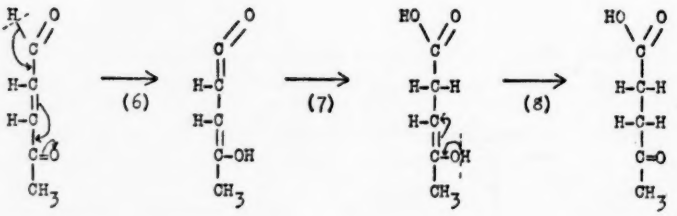
[3] A bibliography on levulinic acid has been prepared by the A. E. Staley Manufacturing Co., Decatur Ill.

Step (1) is somewhat analogous to the conversion of triacetylglucal to diacetylpseudoglucal, (2) is merely a conversion of a hemiacetal to an aldehyde, (3) is a de-enolization, (4) depicts cleavage of a carbon-carbon bond by enolization of a keto group to form a ketene derivative, a process represented as somewhat analogous to enolization through a conjugated double bond. Since the ketene would add a proton and a hydroxyl to give the enolic form of levulinic acid, step (5), it would have only a transitory existence.

Levene and Mori have observed the production of levulinic acid from 2-desoxypentoses [31]; an explanation similar to that given above may be advanced to account for this reaction, formulas LXXXI to LXXXIX. Step 6 is noteworthy as it represents enolization of a keto group through the hydrogen of an aldehyde, a step somewhat analogous to (4) in the preceding process. The existence of LXXXVII as a chemical entity would seem questionable and hence this compound is considered merely as a transition state between the aldehyde and the acid. The transition might follow a free radical course similar to the mechanism of the Cannizzaro reaction.



LXXXI LXXXII LXXXIII LXXXIV LXXXV



LXXXVI LXXXVII LXXXVIII LXXXIX

The examples which have been cited, clearly show how the principle of consecutive electron displacement provides a rational basis for many reactions which have heretofore seemed somewhat peculiar. Naturally all reactions cannot be explained by any one mechanism. Possibly some of the reactions described here may be found in the future to follow other mechanisms, but nevertheless the concept of consecutive electron displacement seems to provide a very useful means for correlating existing knowledge and for stimulating further investigation.

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WASHINGTON, December 12, 1943.

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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1574

Part of Journal of Research of the National Bureau of Standards, Volume 32, February 1944

MEASURING THE RATE OF WEAR OF TIRE TREADS

By Frank L. Roth and William L. Holt

ABSTRACT

The rates of wear of different tread materials were determined by weighing tires after running them prescribed distances on the roads. The method proved feasible for passenger car tires, involved a minimum amount of work, and yielded data in a few miles of driving which could be used to predict the life of the tread. This paper presents typical results obtained on five different tread materials, including prewar natural rubber treads. The rate of wear of the least resistant tread material was eight times that of the most resistant material.

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I. INTRODUCTION

During the height of the emergency period, when many possible materials were being considered for the treads of pneumatic tires, this Bureau was called upon to make measurements on the rate of wear of several of these materials. Since few tires and even fewer test cars were available, and early results were desired, it was necessary to obtain a reasonably precise and reliable measure of the tread wear during relatively few miles of driving. There are two obvious methods of determining the loss of tread rubber from a tire: (1) by measuring the groove depths in the tread design at intervals, and (2) by weighing the tire at intervals.

The first method requires measurements of groove depths at many places on the tire. Since the depths of the grooves in most new passenger car tires are only $\frac{3}{8}$ inch or less and are not uniform in many tread designs, it is clearly difficult, by this method to obtain any reliable prediction about the life of the tread until an appreciable portion of the rubber has been worn away.

The second method, namely, weighing the tire at intervals, was chosen because of the greater precision obtained by its use. The weight of a tire can be determined to within 1 or 2 grams, and about 2,000 grams of tread-rubber are worn away during the life of the tread. Observations of tread wear for these several materials were continued after the preliminary predictions of the tread lives had been made. The results obtained showed that this method was feasible for evaluat-

ing passenger car tires and indicated the effect of other details, such as the location of the tires on the car and the alinement of the wheels. The data presented in this paper illustrate typical results on five different tread materials, including prewar natural rubber treads. The rate of wear of the least resistant tread material was eight times that of the most resistant material.

II. METHOD OF DETERMINING THE RATE OF TREAD WEAR

The tires reported on in this paper were four-ply, size 6.00–16, with highway design treads. Some were recaps and some were new tires. A tire with tube was mounted on a wheel, and the whole assembly was weighed on an equal-arm balance. The weight of a mounted tire and wheel was in the neighborhood of 20,000 grams, and the precision of weighing was 1 gram. The air pressure was always adjusted to 32 lb/in.^{2}, with the tire at room temperature previous to weighing. The wheel assemblies were placed on a test car, and after running them prescribed distances were removed and weighed. For most tires the loss of weight was determined at from 100- to 300-mile intervals, and for some, where the loss was small, at 500- to 1,000-mile intervals.

Usually the tire and wheel were merely brushed clean before weighing them. When it was necessary to wash off mud and dirt, the tires were dried in a warm room (100° F) for about 2 hours before weighing. Judging from the consistency of successive weighings, this washing had little effect on the weight. By using a reference tire and making weighings over a period of 15 months, a gradual change in weight from season to season was noted. The weight was greatest in October and least in March. The difference was about 20 grams and could be attributed to relatively high and low humidities. Such changes in weight due to changes in humidity were small compared with the loss in weight due to wear.

III. CONDITIONS OF TEST

Most of the results reported are based on tests made on a Studebaker Champion coach (abbreviated STUD), but some were made on a Ford coach and a few on a Chevrolet station wagon (abbreviated CHEV). The loads carried by the first two cars varied with the number of passengers. The load carried by the Chevrolet was approximately constant. The loads were as follows:

STUD	Front tires	775 to 800 pounds.
	Rear tires	770 to 910 pounds.
FORD	Front tires	approximately 870 pounds.
	Rear tires	approximately 935 pounds.
CHEV	Front tires	approximately 885 pounds.
	Rear tires	approximately 935 pounds.

The speeds were moderate and seldom exceeded 40 mph. Air pressures were maintained at approximately 32 lb/in^2. The tires were not run over the same route, but the general character of the roads was the same. They were paved for the most part and consisted partly of concrete and partly of macadam. Tests were made at periods between April 1942 and September 1943. More exact dates are given on the graphs for particular tires.

IV. RESULTS

The results of tests are shown in figures 1, 2, and 3. Five different tread materials are considered (1) 100-percent reclaimed rubber, (2) butyl rubber, (3) Flexon, a modified butyl rubber, (4) GR–S type synthetic rubber, and (5) natural rubber.

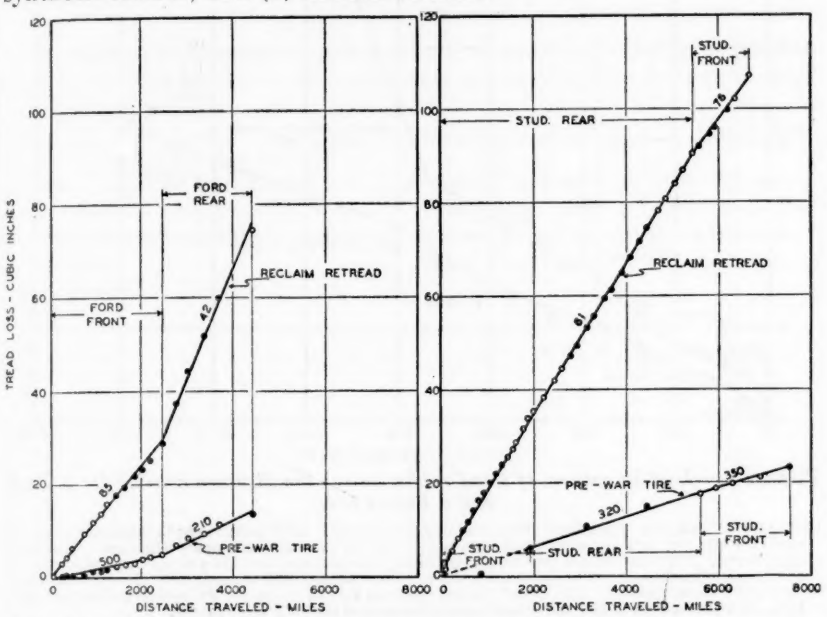

FIGURE 1.—*Loss in volume of tread rubber versus the distance traveled for two 100 percent reclaim recaps and two prewar natural rubber tires.*

Solid points refer to measurements made when the tire was on a left wheel, and open points refer to measurements made when the tire was on a right wheel. The numbers on the straight portions of the curves show the average miles of service per cubic inch of tread wear. The tires were run between April and September 1942.

Because the specific gravities of the tread materials differed, the losses in weight were converted to losses in volume, and these values are plotted against the miles run. The specific gravities as measured were: reclaim, 1.28; butyl rubber, 1.13; Flexon, 1.17; GR–S type, 1.18; natural rubber, 1.14. Lines show the average rate of wear under each test condition, and a number shows the reciprocal of this rate in miles per cubic inch of rubber. The range of these values is given in table 1.

TABLE 1.—*Range of values for different treads*

Kind of tread	Miles per cubic inch of tread wear [a]
Prewar (natural rubber)	210 to 350 [b]
GR–S type	210 to 320
Butyl rubber	150 to 280
Flexon	120 to 260
Reclaim	42 to 85

[a] For a 6.00–16 tire there are usually about 100 cubic inches of tread available, so that the figures in the table may be multiplied by 100 to obtain an approximation of the total miles of service from a tread.

[b] The value of 500 miles obtained for the front wheel of the Ford (fig. 1) was probably due to exceptionally favorable conditions.

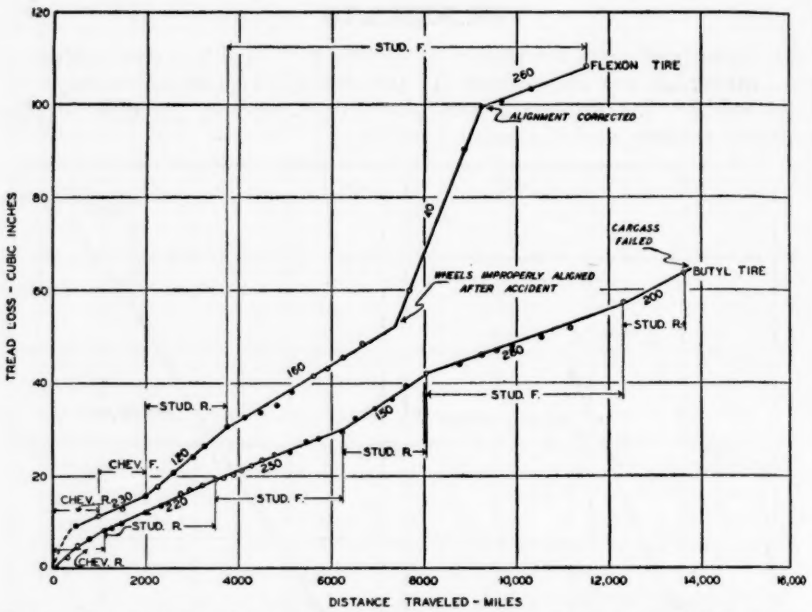

FIGURE 2.—*Loss in volume of tread rubber versus the distance traveled for a Butyl and a Flexon tire.*

"F" and "R" indicate, respectively, front and rear wheel wear. Solid points refer to measurements made when the tire was on a left wheel, and open points refer to measurements made when the tire was on a right wheel. The numbers on the straight portions of the curves show the average miles of service per cubic inch of tread wear. The Flexon tire was run from August 1942 to April 1943. It was on the front during the winter months. The Butyl tire was run from July to December 1942 and from May to August 1943. It was removed during the winter months because of poor traction in snow.

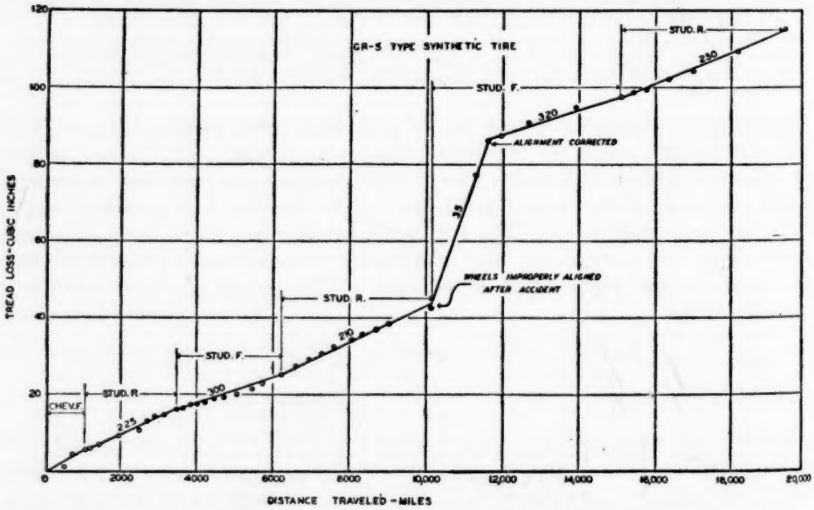

FIGURE 3.—*Loss in volume of tread rubber versus the distance traveled for a GR-S type synthetic tire.*

"F" and "R" indicate, respectively, front and rear wheel wear. Solid points refer to measurements made when the tire was on a left wheel, and open points refer to measurements made when the tire was on a right wheel. The numbers on the straight portion of the curves show the average miles of service per cubic inch of tread wear. The tire was run from July 1942 to September 1943.

A record of the daily temperatures was kept during the time some of the tires were being run, and an attempt was made to correlate wear with temperature. No marked difference was found in the rate of wear during periods of relatively high or low temperatures.

V. CONCLUSIONS

The method of determining the rate of wear of tire treads by weighing the tire and wheel at intervals and noting the loss in weight has been found feasible for passenger car tires.

Data on the rate of wear can be obtained from a tire which has run comparatively few miles.

This method is quite sensitive in showing up features that influence wear, such as differences between front and rear wheels and the effect of misalinement.

WASHINGTON, November 24, 1943.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1575

Part of Journal of Research of the National Bureau of Standards, Volume 32, February 1944

A PRECISION APPARATUS FOR THE RAPID DETERMINATION OF INDICES OF REFRACTION AND DISPERSION BY IMMERSION

By Conrad A. Faick and Bernard Fonoroff

ABSTRACT

A new immersion method for determining indices of refraction and ν values, employing the double-diaphragm method for securing oblique illumination, is described. The average error in the determination of indices of refraction based upon 144 measurements is 2×10^{-5}; the maximum error is 5×10^{-5}. Complete measurements of the indices of refraction for the sodium *D* line and the hydrogen *F* and *C* lines may be made in approximately 1½ hours, and from these measurements the ν values may be calculated with an average error of 0.1 and a maximum error of 0.8.

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I. INTRODUCTION

In the production of optical glass, careful control over the optical properties, especially the index of refraction (n_D) and the Abbe value (ν), of the product is essential. Most methods for measuring indices of refraction are sufficiently accurate for the control of the n_D value. The ν value, on the other hand, presents a special problem in index measurement. It is defined as $(n_D-1)/(n_F-n_C)$, and in order to determine this value within certain specified limits, the index of refraction must be measured very accurately. Some typical tolerances which have to be met and the errors in the index measurements corresponding to these tolerances are shown in table 1.

TABLE 1.—*Typical tolerances for n_D and ν values*

Glass	Typical values and tolerances		Error corresponding to tolerance in ν
	n_D	ν	
Borosilicate crown	1.517 ±0.001	64.5 ±0.3	$\pm2\times10^{-5}$
Light barium crown	1.572 ±0.001	57.4 ±0.3	$\pm3\times10^{-5}$
Dense flint	1.649 ±0.0015	33.8 ±0.3	$\pm9\times10^{-5}$

It is obvious from table 1 that the required accuracy of index measurements is determined mainly by the ν value tolerances. If the errors in index measurements are as great as those listed in column three, the ν value may be in error by the amount of the permissible tolerances. In order to be certain that the ν values are well within the required limits, the best spectrometer measurements [1] are necessary for final control of crown glasses, and are desirable for flint glasses. However, there are many useful routine checks and measurements that can be made on refractometers.

In normal times at the optical glass plant of the National Bureau of Standards, the problem of control was solved by making two independent sets of measurements. The immersion method of Faick and Finn [2] was used for immediate production control work. The final and more accurate values of optical constants were later measured on a spectrometer and a precision refractometer.

During wartime, manufacturers are called upon to make new glasses and a greater variety of them. This requires frequent changes in batch compositions and makes necessary more frequent and careful determination of index of refraction and dispersion. Under these conditions the above-mentioned immersion control method was deficient both as to speed and accuracy. The more accurate index measurements as they are generally made, on spectrometers or on carefully calibrated Pulfrich refractometers, require ground and pitch-polished samples. The time-consuming operations of grinding and polishing cause delay in the processing of the glass or in the revision of batch compositions, especially in glass plants that are not equipped with grinding and polishing facilities for the preparation of samples. Most immersion methods permit the use of rough, unprepared samples, but either do not yield sufficiently accurate results or lack the simplicity and speed desired.[3] It was, therefore, felt desirable to develop an immersion method for rough samples which would have the required accuracy and permit speed and ease of manipulation.

II. METHOD OF MATCHING

One of the chief requirements of immersion refractometry is a sensitive method for ascertaining the match between the indices of the sample and the immersion liquid. Of the various methods that could be used for this, one embodying the principles of oblique illumination, well-known to petrographers, seemed the most promising both for sensitivity and simplicity of operation. A system of oblique illumination, using double diaphragms, has been described by Saylor [4] and shown to be superior to usual methods, at least when used on a microscope. Another double-diaphragm method, employing a telescope and a long focus lens as parts of the optical system, has been used by Cheshire [5] for measuring the index of refraction of glass by immersion. This system is too cumbersome for rapid control work.

[1] H. L. Gurewitz and L. W. Tilton, J. Research NBS **32**, 39 (1944) RP1572.

[2] C. A. Faick and A. N. Finn, BS J. Research **6**, 993–1002 (1931) RP320.
This method consists essentially in matching the index of refraction of the glass with that of a suitable liquid in which the sample is immersed and then measuring the index of the liquid. The apparatus consists of a telescope and a grid, illuminated by a sodium light, which are placed on opposite sides of a water-cooled tank containing the immersion liquid and sample. The match between the glass and the liquid is obtained by altering the index of the liquid until no distortion of the grid pattern is observed through the telescope. Accuracies within $\pm 3\times10^{-4}$ are obtainable with this method.

[3] For a discussion of immersion refractometry, see Glazebrook's Dictionary of Applied Physics **4**, 130 (The Macmillan Co., New York, N. Y., 1923).

[4] C. P. Saylor, J. Research NBS **15**, 277–294 (1935) RP829.

[5] R. W. Cheshire, Phil. Mag. [6] **32**, 409–420 (1916).

Basically, the method finally chosen consists in inserting at the focus of a condensing lens (fig. 1, A) a diaphragm which shades out almost one-half of the beam of light. The emerging beam is then passed through the immersion liquid and again brought to a focus by means of a second converging lens. At this focus (fig. 1, B) a second

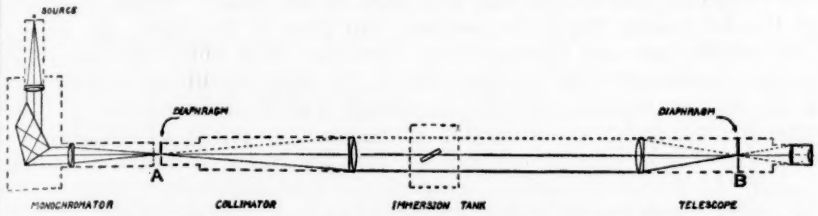

FIGURE 1.—*Schematic drawing of the optical system for matching the indices of the glass and immersion liquid.*

diaphragm is placed so that most of the remaining bright portion of the beam is shaded out. If a telescope is then inserted in the system, the field, as seen through the eyepiece, will appear dimly but uniformly lighted. Now, when a specimen is immersed in a liquid of the same index of refraction as that of the specimen, the light rays passing through the specimen will not be deviated and, since the second

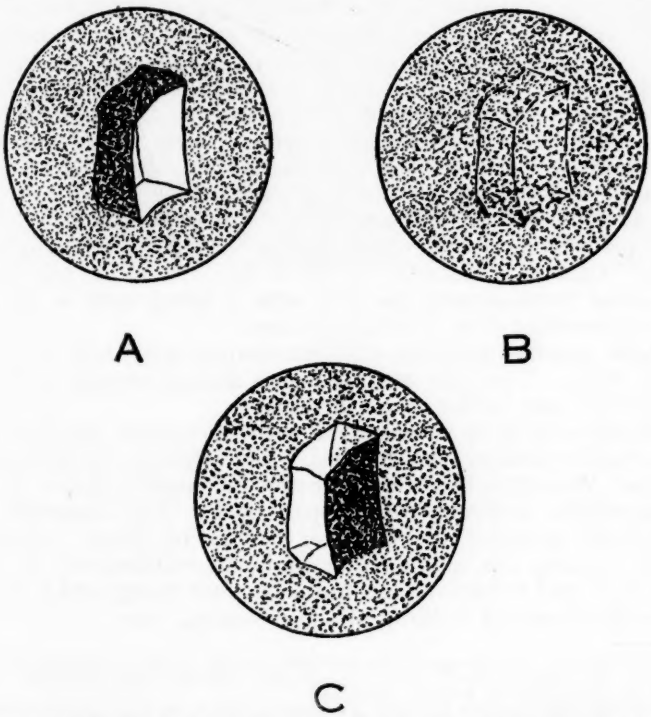

FIGURE 2.—*Field through the eyepiece of the telescope—diaphragm on right side of the instrument.*

A, When the index of the liquid is greater than the index of the sample; B, When the liquid and sample have the same index; C, When the index of the liquid is lower than that of the sample.

diaphragm takes out the bright portion of the beam, the sample will be practically invisible against the dimly lighted field seen through the eyepiece (fig. 2, B). However, if the match between the sample and liquid is altered, the path of light passing through the sample will be deviated so that the sample no longer blends with the field, but becomes light on one side and dark on the other. When the index of the immersion liquid is greater than that of the glass, the side of the sample (as seen through the telescope) that is on the same side as the diaphragms will be light (fig. 2, A); when the index of the liquid is lower, the opposite side of the sample will be light (fig. 2, C). By altering the index of refraction of the immersion liquid, which is a mixture of two liquids, one of a low and the other of a high refractive index, the match between the specimen and immersion medium can be easily established. After a match has been obtained, the index of refraction of the liquid is measured on a precision refractometer by comparison with a standard of approximately the same index.

III. APPARATUS

The apparatus (figs. 1 and 3) consists essentially of light sources, a monochromator with the exit slit removed, a collimator, an immersion tank, a telescope, a tested precision refractometer, and accessory equipment. Referring to figure 1, the light from the source is first passed through a monochromator,[6] where a particular spectrum line is isolated and is brought to a focus at the end of the collimator where the first diaphragm is placed. This diaphragm is an adjustable knife-edge that covers part of a circular opening, replacing the usual collimator slit. The light then passes through the collimator, from which it emerges as a parallel beam (or a very slightly converging one) that passes through the tank and then enters the telescope. Near the focal plane, the second diaphragm, which is also adjustable, is located. The objective is selected so that in combination with the eyepiece it forms a telescope that can be focused on the sample in the immersion tank at a distance which is convenient for the operator. As an added convenience, the telescope is fitted with a right-angle prism and mounted in a vertical position.

The light sources used are a sodium-vapor lamp and a hydrogen-discharge tube. They are mounted on a sliding support to facilitate changing from one to the other (fig. 3).

The immersion tank is equipped with plate-glass windows and a water jacket for temperature control. The water jackets of this tank and of the refractometer are connected in parallel, and water from the same source is circulated through both. The accessory equipment includes a water reservoir and circulating pump, a motorized stirrer for mixing the immersion liquids, thermometers[7] in the immersion tank and refractometer and a vacuum pump and a hydrogen generator for frequent refilling of the discharge tube.

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[6] By use of a monochromator, it was possible to avoid difficulties arising from the other lines in the sodium source, and from the continuous spectrum in the hydrogen tube. Filters like those used on the refractometer were found unsatisfactory on the matching instrument.

[7] Mercury-in-glass type graduated to a tenth of a degree, permitting the estimation of hundredths of a degree. The thermometers should be carefully checked against each other, since the difference in temperature is the important factor.

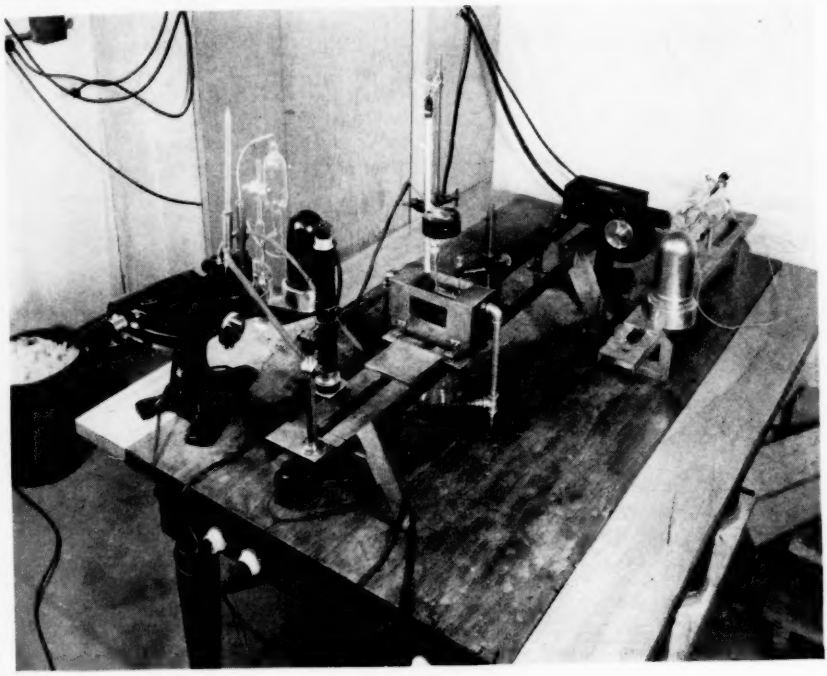

FIGURE 3.—*Complete immersion apparatus.*

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IV. PROCEDURE

Six immersion liquids were prepared. The indices of refraction of these liquids were approximately 1.517, 1.572, 1.604, 1.617, 1.620, and 1.649, respectively. The first five liquids were mixtures of liquid petrolatum (n_D=1.456) and α-chloronaphthalene (n_D=1.632). The sixth liquid was a mixture of α-chloronaphthalene and α-bromonaphthalene (n_D=1.656). After isolating a particular spectrum line by means of the monochromator, the sample was immersed in the appropriate liquid, and the two were matched for index by adding small quantities of one of the pure liquids. When a good match had been obtained, the index of the immersion liquid was measured on the refractometer. This process was repeated four times for each sample. In each series of measurements, care was taken to approach the correct value from both a higher index immersion liquid and a lower one. Measurements of the temperature of the immersion liquid and of the refractometer prism block were made with a precision of $\pm 0.02°$ C. Corrections for very small temperature differences were applied by using an average change of -0.00035 in index per degree rise in temperature.

In order to obtain the highest possible accuracy in index measurements, a comparison method recommended by Tilton[8], was used. By this method, instrumental errors, such as a shift in the zero setting, can be readily compensated. Essentially this method consists in checking the refractometer, before and after each series of immersion measurements, with a standard of known index approximately the same as the rough sample being measured and making the necessary corrections. This check was made for each type of glass and for each wavelength used, by measuring the standard as a Pulfrich slab on the refractometer. In several cases brought to the attention of the authors, considerable difference was found in the readings of refractometers when measuring solid and liquid samples of the same index. Should this be the case, an alternative procedure should be used in checking the refractometer. In the alternative procedure a liquid which in each case is matched with a known sample in index is used as the "standard" instead of the solid sample.

A series of 12 glass samples was tested to obtain the accuracy of the instrument. These samples were cut from prisms that had been previously measured on a spectrometer. The indices of refraction of these test pieces were known to the fifth decimal place. Since these samples were in the shape of rectangular prisms approximately 2 by 2 by 0.2 cm in size and had polished faces, and since the instrument was designed for measuring rough, irregularly shaped specimens, it was necessary to compare the accuracies of measurement obtainable with rough pieces and finished samples. This was done by measuring the indices of refraction of four rough pieces of glass and then grinding these pieces to the same shape as the standards and then remeasuring the indices. The results of this test show that any difference that does exist is within the error of measurement.

[8] L. W. Tilton, J. Opt. Soc. Am. **32**, 371–381 (1942).

TABLE 2.—*Comparison of measurements made on rough, irregularly shaped samples and on fine-ground, rectangular specimens*

Index of refraction (n_D)			Index of refraction (n_D)		
Rough sample		Ground sample	Rough sample		Ground sample
SAMPLE I			SAMPLE III		
1	1.51580	1.51578	1	1.60179	1.60178
2	1.51582	1.51581	2	1.60182	1.60180
3	1.51578	1.51583	3	1.60180	1.60180
4	1.51585	1.51580	4	1.60184	1.60181
Average	1.51581	1.51581	Average	1.60181	1.60180
SAMPLE II			SAMPLE IV		
1	1.57187	1.57188	1	1.61960	1.61960
2	1.57189	1.57187	2	1.61961	1.61963
3	1.57190	1.57186	3	1.61963	1.61961
4	1.57188	1.57190	4	1.61962	1.61962
Average	1.57189	1.57188	Average	1.61962	1.61962

V. RESULTS

The values obtained in the test of the rough blanks are given in table 2. A total of 48 measurements were made on the 12 regular samples for each of the wavelengths, corresponding to the sodium *D* line, and hydrogen *F* and *C* lines. The results of these measurements are tabulated in table 3. Table 3 also shows the errors in the measured

TABLE 3.—*Comparison of immersion determinations of index of refraction and dispersion with spectrometer values*

Method	n_D	Error $\times 10^5$	n_F	Error $\times 10^5$	n_C	Error $\times 10^5$	μ	Error
SAMPLE I								
Spectrometer	1.51651		1.52211		1.51411		64.6	
Immersion 1	1.51653	+2	1.52213	+2	1.51412	+1	64.6	0
Immersion 2	1.51653	+2	1.52209	−2	1.51413	+2	64.9	+0.3
Immersion 3	1.51650	−1	1.52210	−1	1.51410	−1	64.6	0
Immersion 4	1.51651	0	1.52208	−3	1.51412	+1	64.9	+.3
Average	1.51652	1	1.52210	2	1.51412	1	64.8	0.2
SAMPLE II								
Spectrometer	1.51748		1.52316		1.51507		64.0	
Immersion 1	1.51746	−2	1.52318	+2	1.51509	+2	64.0	0
Immersion 2	1.51747	−1	1.52316	0	1.51510	+3	64.2	+0.2
Immersion 3	1.51750	+2	1.52317	+1	1.51508	+1	64.0	0
Immersion 4	1.51746	−2	1.52313	−3	1.51508	+1	64.3	+.3
Average	1.51747	2	1.52316	2	1.51509	2	64.1	0.1
SAMPLE III								
Spectrometer	1.57205		1.57906		1.56913		57.6	
Immersion 1	1.57202	−3	1.57909	+3	1.56914	+1	57.5	−0.1
Immersion 2	1.57202	−3	1.57904	−2	1.56909	−4	57.5	−.1
Immersion 3	1.57206	+1	1.57905	−1	1.56911	−2	57.6	0
Immersion 4	1.57206	+1	1.57906	0	1.56911	−2	57.5	−.1
Average	1.57204	2	1.57906	2	1.56911	2	57.5	0.1

TABLE 3.—*Comparison of immersion determinations of index of refraction and dispersion with spectrometer values*—Continued

Determination	n_D	Error $\times 10^5$	n_F	Error $\times 10^5$	n_C	Error $\times 10^5$	ν	Error
SAMPLE IV								
Spectrometer	1.57151		1.57850		1.56859		57.7	
Immersion 1	1.57150	−1	1.57849	−1	1.56858	−1	57.7	0
Immersion 2	1.57151	0	1.57853	+3	1.56860	+1	57.6	−0.1
Immersion 3	1.57154	+3	1.57847	−3	1.56861	+2	58.0	+.3
Immersion 4	1.57151	0	1.57846	−4	1.56858	−1	57.8	+.1
Average	1.57152	1	1.57849	3	1.56859	1	57.8	0.1
SAMPLE V								
Spectrometer	1.60428		1.61419		1.60027		43.4	
Immersion 1	1.60431	+3	1.61416	−3	1.60025	−2	43.4	0
Immersion 2	1.60430	+2	1.61416	−3	1.60024	−3	43.4	0
Immersion 3	1.60431	+3	1.61420	+1	1.60023	−4	43.3	−0.1
Immersion 4	1.60428	0	1.61419	0	1.60028	+1	43.4	0
Average	1.60430	2	1.61418	2	1.60025	3	43.4	0
SAMPLE VI								
Spectrometer	1.60454		1.61446		1.60053		43.4	
Immersion 1	1.60454	0	1.61450	+4	1.60056	+3	43.4	0
Immersion 2	1.60457	+3	1.61449	+3	1.60054	+1	43.3	−0.1
Immersion 3	1.60456	+2	1.61450	+4	1.60053	0	43.3	−.1
Immersion 4	1.60454	0	1.61447	+1	1.60057	+4	43.5	+.1
Average	1.60455	1	1.61449	3	1.60055	2	43.4	0.1
SAMPLE VII								
Spectrometer	1.61804		1.63018		1.61320		36.4	
Immersion 1	1.61804	0	1.63020	+2	1.61322	+2	36.4	0
Immersion 2	1.61803	−1	1.63019	+1	1.61323	+3	36.4	0
Immersion 3	1.61801	−3	1.63019	+1	1.61324	+4	36.5	+0.1
Immersion 4	1.61806	+2	1.63017	−1	1.61325	+5	36.5	+.1
Average	1.61804	2	1.63019	1	1.61324	3	36.5	0.1
SAMPLE VIII								
Spectrometer	1.61731		1.62942		1.61249		36.5	
Immersion 1	1.61734	+3	1.62941	−1	1.61250	+1	36.5	0
Immersion 2	1.61729	−2	1.62943	+1	1.61252	+3	36.5	0
Immersion 3	1.61728	−3	1.62937	−5	1.61252	+3	36.6	+.1
Immersion 4	1.61729	−2	1.62940	−2	1.61252	+3	36.6	+.1
Average	1.61730	3	1.62940	2	1.61252	3	36.6	.1
SAMPLE IX								
Spectrometer	1.62024		1.63248		1.61536		36.2	
Immersion 1	1.62023	−1	1.63249	+1	1.61536	0	36.2	0
Immersion 2	1.62024	0	1.63251	+3	1.61536	0	36.2	0
Immersion 3	1.62027	+3	1.63252	+4	1.61540	+4	36.2	0
Immersion 4	1.62027	+3	1.63246	−2	1.61539	+3	36.3	+0.1
Average	1.62025	2	1.63250	3	1.61538	2	36.2	0
SAMPLE X								
Spectrometer	1.62023		1.63247		1.61536		36.2	
Immersion 1	1.62022	−1	1.63246	−1	1.61539	+3	36.3	+0.1
Immersion 2	1.62024	+1	1.63247	0	1.61535	−1	36.2	0
Immersion 3	1.62025	+2	1.63242	−5	1.61537	+1	36.4	+.2
Immersion 4	1.62025	+2	1.63248	+1	1.61536	0	36.2	0
Average	1.62024	2	1.63246	2	1.61537	2	36.3	+0.1

TABLE 3.—*Comparison of immersion determinations of index of refraction and dispersion with spectrometer values*—Continued

Method	n_D	Error $\times 10^5$	n_F	Error $\times 10^5$	n_C	Error $\times 10^5$	μ	Error
SAMPLE XI								
Spectrometer	1.64918		1.66296		1.64373		33.8	
Immersion 1	1.64918	0	1.66300	+4	1.64375	+2	33.7	−0.1
Immersion 2	1.64917	−1	1.66296	0	1.64370	−3	33.7	−.1
Immersion 3	1.64915	−3	1.66296	0	1.64371	−2	33.7	−.1
Immersion 4	1.64917	−1	1.66293	−3	1.64373	0	33.8	0
Average	1.64917	1	1.66296	2	1.64372	2	33.7	0.1
SAMPLE XII								
Spectrometer	1.64845		1.66220		1.64301		33.8	
Immersion 1	1.64845	0	1.66215	−5	1.64301	0	33.9	+0.1
Immersion 2	1.64847	+2	1.66217	−3	1.64299	−2	33.8	0
Immersion 3	1.64842	−3	1.66218	−2	1.64296	−5	33.7	−.1
Immersion 4	1.64845	0	1.66218	−2	1.64306	+5	33.9	+.1
Average	1.64845	1	1.66217	3	1.64300	3	33.8	0.1

values as compared with the spectrometer values. An examination of these errors shows that the maximum error, or degree of accuracy, for any single measurement is $\pm 5 \times 10^{-5}$, but the average error for the 144 measurements is only $\pm 1.9 \times 10^{-5}$. The reproducibility, or precision, of these measurements, expressed as the average of the deviations from the mean value of each set of four immersion measurements, is $\pm 1.5 \times 10^{-5}$.

A summary of the average accuracy and precision of all the determinations is given in table 4.

TABLE 4.—*Summary of accuracy and precision of determinations listed in table 3*

	Average error	Average deviation from mean values
n_D	1.6×10^{-5}	1.4×10^{-5}
n_F	2.1×10^{-5}	1.6×10^{-5}
n_C	2.1×10^{-5}	1.6×10^{-5}
All values	1.9×10^{-5}	1.5×10^{-5}

The accuracy attained in these measurements is almost as high as the precision attainable on a refractometer. This indicates that the errors introduced in determining the match between the indices of the glass and liquid are for the most part negligible. According to Tilton,[9] it would be very difficult to obtain results of this accuracy without the strict use of a comparison or substitution method. The success attained may be largely attributed to the fact that in measuring a known standard, on the refractometer both before and after each group of four immersion measurements, a comparison method was used that approximates a substitution method. Other factors which should be mentioned are (1) temperature differences between the refractometer and immersion tank were rarely greater than 0.1°, and these temperature effects were considered in obtaining the final

[9] L. W. Tilton, J. Research NBS **30**, 311–328 (1943) RP1535.

values, and (2) the recommended tests to eliminate shielding of rays, setting on false edges, etc. (see footnote 9) were frequently made.

Although the errors introduced in matching are, in general, negligible, the experience of the operator plays a part in these determinations. This is due to surface effects that interfere with the determination of a match. The ideal condition is one which produces a uniformly illuminated field against which the sample is invisible. This exists very rarely in actual practice. Usually, under conditions of match, the main body of the sample will blend with the field, but the edges of the sample will be outlined by very thin brilliant lines. In these cases, a match is determined by rotating the sample through 180°. There should be no change in the thickness or brilliance of these lines when this is done. Thus any confusion due to surface effects may be avoided. The experience of the operator will also determine the speed with which measurements are made. An experienced person can measure about six samples in an 8-hour day. Thus it is possible to secure complete information on the index of refraction and ν value for a particular melt within 1½ hours after a pot of glass is opened.

VI. SUMMARY

An improved apparatus for determining indices of refraction and dispersion of glass by immersion is described. The results of 144 measurements indicate that the index of refraction may be determined with an average error of $\pm 1.9 \times 10^{-5}$ and a maximum error of $\pm 5 \times 10^{-5}$. Dispersion as represented by ν values may be calculated from these measurements with an average error of 0.1 and a maximum error of 0.8. This apparatus may, therefore, be used both for routine production control work and for the determination of the optical constants of finished optical components, especially of flint glasses. It may also be applied profitably to research in the determination of the effect of composition on the optical properties of glass, especially where the glasses studied may be unstable. The full possibilities of the matching instrument have not been determined. More accurate refractometers and temperature controls are necessary for this purpose.

WASHINGTON, October 1, 1943.

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